ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 6, pp. 1216–1221. © Pleiades Publishing, Ltd., 2011.
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Amidation of the Ester Group of Methylpheoforbide *a* with Sterically Nonhindered Primary and Secondary Aliphatic Amines

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Received May 25, 2010

Abstract—It is shown that the reaction of methylpheoforbide *a* with a series of primary and secondary aliphatic amines at elevated temperature (boiling in toluene) leads to the amidation of carbomethoxy group in the position 13(2) of the methylpheoforbide *a* exocycle instead of the cleavage of exocycle with the formation of the corresponding 13-amides of the chlorin e_6. Possible reasons of the observed change in the reaction pathway are presented.

DOI: 10.1134/S1070363211060259

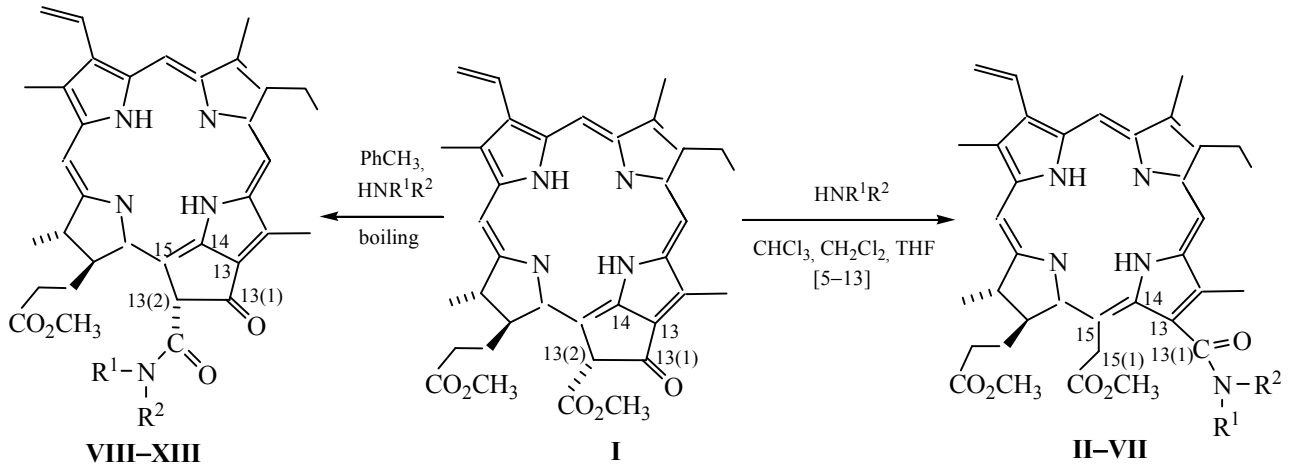
The development of methods of chemical modification of such derivatives of chlorophyll *a* like methylpheoforbide *a* **I** (Scheme 1) presents great interest in connection with the promising use of the chlorins obtained as antitumor preparations [1–3]. The exocycle of the compound **I** and its analogs is an active fragment entering various reactions. Many of them are used for the synthesis of the chlorin derivatives [4–13]. As is known, treating of methylpheoforbide *a* **I** with primary and secondary amines may proceed as the exocycle opening to give 13-amides of the chlorin e_6 [4–11] as well as the amidation of carbomethoxy group in the position 13(2) [12].

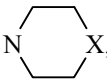
In the case of amines having bulky substituents at nitrogen (dibutylamine, dihexylamine, dioctylamine, etc.) the cleavage of exocycle is impossible due to the sterical hindrances to the nucleophilic attack by the amine of the carbonyl group in the position 13(1) [12]. While boiling methylpheoforbide *a* **I** with such sterically hindered amines in toluene or DMF the amidation of carbomethoxy group in the position 13(2) takes place [12]. The cleavage of exocycle of methylpheoforbide *a* **I** with the sterically non-hindered amines takes place at room temperature or while boiling in low boiling solvents like chloroform, methylene chloride or THF [8, 9, 12, 13] as in the case of formation of the products **II–VII** (Scheme 1). In [4–6, 9–11] describing the exocycle opening under the action of the amine excess on compound **I** is not mentioned the formation of the products of amidation of 13(2)-CO_2CH_3 group. While preparing the analogous compounds in the course of our studies [7, 8, 12, 13] no formation of such compounds was also observed.

In this work the reaction of methylpheoforbide *a* **I** with a series of the sterically nonhindered primary and secondary amines was studied under the conditions providing the amidation of the ester group of exocycle with the sterically hindered amines (in toluene at boiling). The constant high temperature in the course of the process is maintained by slowly adding a solution of amine in toluene to the boiling solution of methylpheoforbide *a* **I** in the same solvent.

The change in the reaction conditions causes the change in its direction. Instead of opening the exocycle which is not sterically hindered now, the amidation of the ester group of methylpheoforbide *a* **I** in the position 13(2) takes place (see Scheme 1, compounds **VIII–XIII**). The structure of the 13(2)-amides **VIII–XIII** obtained was confirmed by the IR and ^{1}H NMR data. In the IR spectra of these substances a band

Scheme 1.



NR^1R^2: $HN(CH_2)_nCH_3$, n = 3 (**II, VIII**), 5 (**III, IX**), 7 (**IV, X**); $N(C_2H_5)_2$ (**V, XI**);  , X = CH_2 (**VI, XII**), O (**VII, XIII**).

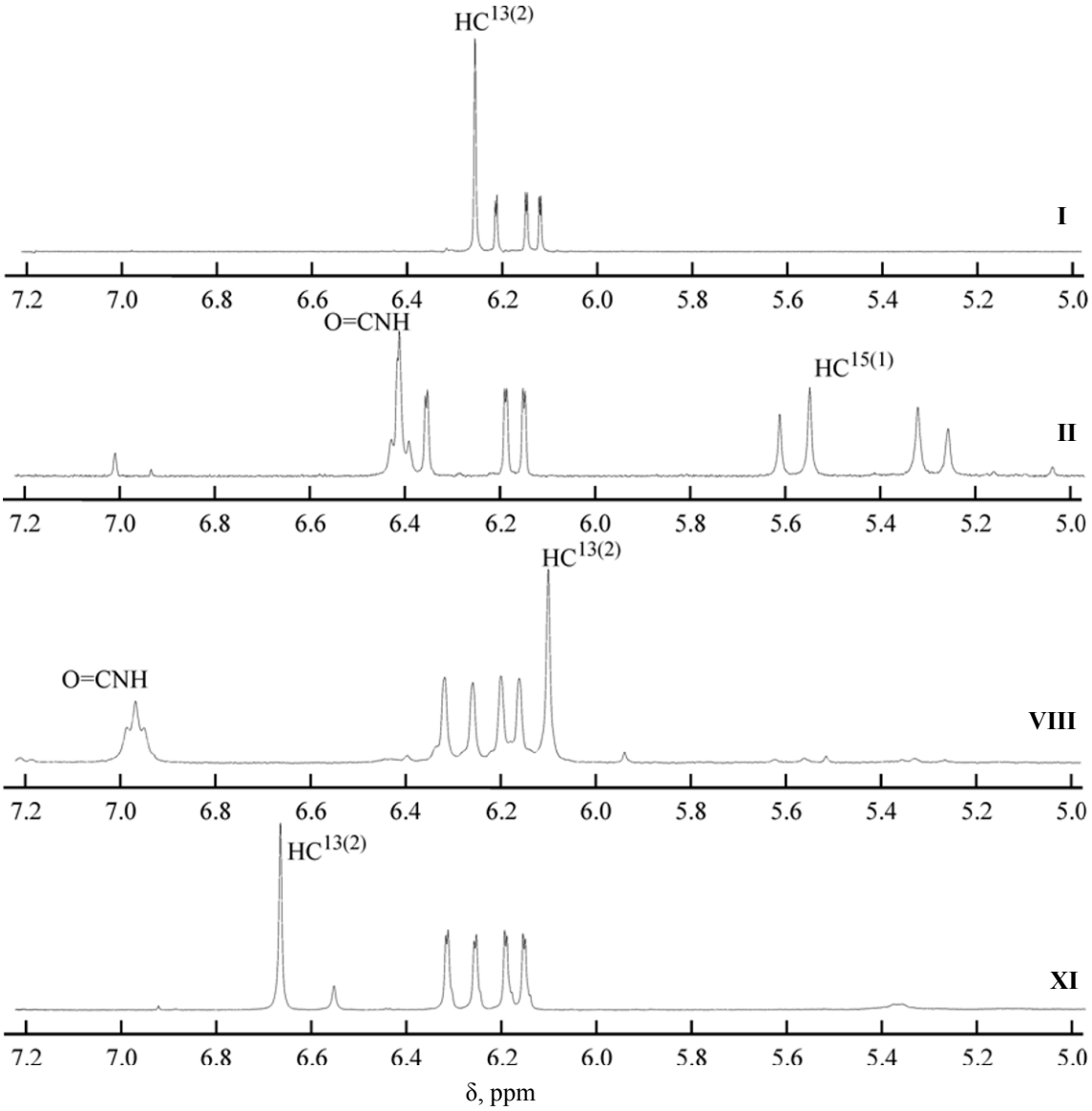
remains corresponding to the absorption of the carbonyl group in the position 13(1) which confirms the retention of the exocycle. In the products of reaction of the exocycle cleavage no such band would appear [7, 8]. The presence of the exocycle in compounds **VIII–XIII** is confirmed also by the ^{1}H NMR data. In the spectra of the compounds obtained a singlet of proton in the position 13(2) of exocycle is observed. In the spectra of the chlorin e_6 13-amides such singlet is absent. Instead of that the multiplet is present of the AB-system corresponding to the methylene group in the position 15(1) resulting from the exocycle cleavage [7, 8] (see the figure).

The presence of exocycle in compounds **VIII–XIII** is confirmed indirectly also by the values of chemical shifts of the NH-protons of the chlorin macrocycle. The signal of NH-proton in compounds **VIII–XIII** appears in a relatively weak field (0.4–0.5 ppm) same as in the case of methylpheoforbide *a* **I.** In the chlorophyll derivatives without exocycle the signal of this proton is observed at –1.5 to –1.7 ppm [7, 8]. The amido group of the compounds obtained is characterized in the IR spectra by the band at 1659–1620 cm^{-1} for all the amides ("amide I band") and the band at 1550–1551 cm^{-1} ("amide II band") in the case of secondary amides **VIII–X**. In the ^{1}H NMR spectra the signals of protons of substituents at the nitrogen and the signals of the amide NH-protons in the case of secondary amines are observed.

The molecule of methylpheoforbide *a* **I** contains two ester groups [in the position 13(2) of exocycle and in methyl propionate fragment in the position 17] which can take part in the reaction with amine. The fact that the reaction occurred at the ester group of exocycle [in the position 13(2)] was established on the basis of following data. In the ^{1}H NMR spectra of the com-pounds obtained a singlet at 3.91 ppm belonging to the methoxy group of the ester fragment in the position 13(2) is absent indicating its substitution (see the figure). Besides, the signal of proton in the position 13(2) is shifted considerably as compared to the analogous signal in the spectrum of methylpheoforbide *a* **I** because of the insertion of a bulky amido group in the position 13(2) (see the figure). It is interesting, that in tertiary amide the signal of this proton is shifted downfield, while in secondary amides the upfield shift takes place. Considerably larger shift in the case of tertiary amides is caused evidently by the larger size of substutuents adjacent to the exocycle, and hence to its greater distortion.

Higher activity of ester group in the position 13(2) in the reaction with amines may be explained by the ability of the hydroxy group of the enol form of methylpheoforbide *a* **I** to form hydrogen bond with the carbonyl oxygen of the ester group in the position 13(2) increasing the partial positive charge on the carbonyl carbon atom and facilitating the nucleophilic attack on this atom (Scheme 2).

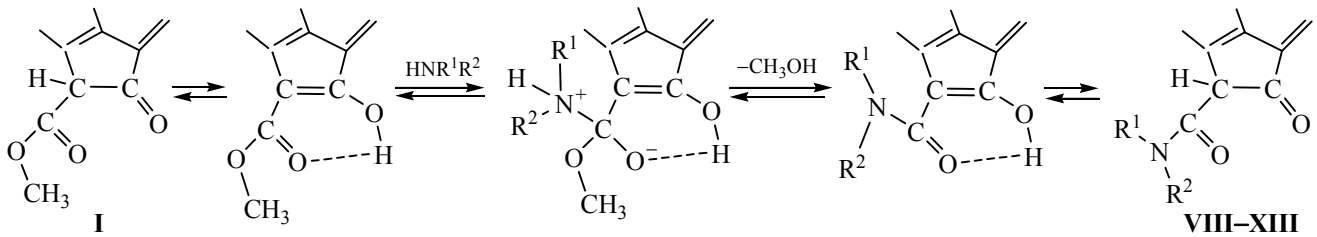
Hence, methylpheoforbide *a* **I** reacts with primary and secondary amines at elevated temperature to form carboxamides from carbomethoxy group in the position 13(2) instead of the cleavage of the exocycle.



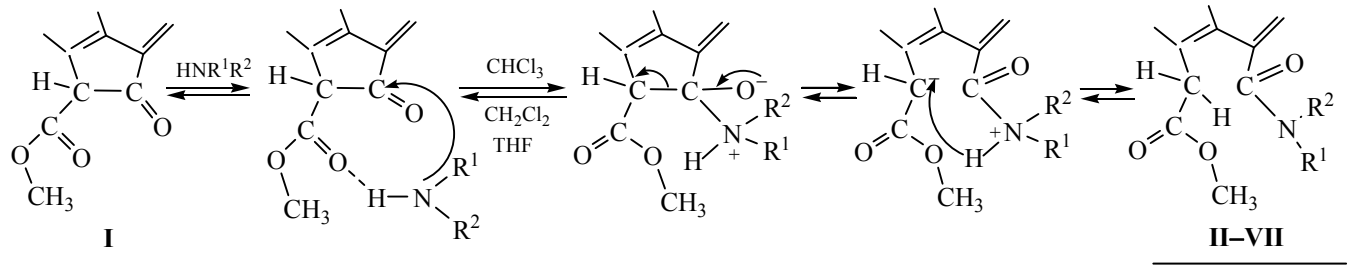
^{1}H NMR spectrum of methylpheoforbide *a* **I** and the products of its reaction with butylamine and diethylamine (5.0–7.2 ppm, $CDCl_3$, 300 MHz).

The change in the reaction pathway may be connected with the specific features of methylpheoforbide *a* **I** exocycle as an object of the nucleophilic attack. It seems quite possible that the molecule of amine forms hydrogen bond with the ester group in the position 13(2) (Scheme 3). Such interaction favors the nucleophilic attack of keto group in the position 13(1) because it holds the amine molecule near the object of attack and

Scheme 2.



Scheme 3.



to some extent increases the partial negative charge on the amine nitrogen atom. The increase in temperature prevents the formation of this intermolecular hydrogen bond.

Hence, increase in temperature considerably decreases the effect of factors favorable for the exocycle opening and leads to amidation of the ester group of methylpheoforbide *a* **I** exocycle.

EXPERIMENTAL

^{1}H NMR spectra were taken on a Bruker Avance II (300 MHz) spectrometer in $CDCl_3$. Mass spectra were registered on a Vision 2000 spectrometer (MALDI in dihydroxybenzoic matrix). IR spectra were obtained on an IR Prestige 21 device (diffuse reflection, KBr powder). TLC was carried out on Silufol plates, elution with CCl_4-acetone mixture, 1:4 vol/vol. Column chromatography was carried out on an L 100/400μ silica gel (wet filling). Methylpheoforbide *a* **I** was isolated from spirulina microalgae, the representative of *Cyanophyceae* according to [15]. Spectral characteristics of compound **I** were analogous to that reported previously [8]. Amides **II–VII** necessary for comparison of chromatographic characteristics were prepared according to the previously reported procedures [8, 9, 12, 13].

Methylpheoforbide 13(2)-amides (VIII–XIII) (*general procedure*). To the boiling solution of 0.032–0.08 mmol of compound **I** in 10 ml of toluene a solution of 30–90 mmol of amine in 3 ml of toluene was added. The mixture obtained was refluxed for 1.5–2 h until the completion of the reaction (TLC control), cooled, and washed in the separating funnel at first with 1% hydrochloric acid for removing amine and then with water until the neutral reaction of water layer. The toluene solution obtained was dried over the anhydrous sodium sulfate, and the obtained mixture of chlorins was placed in the silica gel column as a toluene solution and then subjected to gradient elution with CCl_4–acetone mixture increasing gradually the content of the latter.

Methylpheoforbide *a* 13(2)-*N*-butylamide (VIII). Amide **VIII**, 40 mg (74% yield), was obtained as a dark blue powder by treating 50 mg of methylpheoforbide *a* **I** with 0.3 ml of *N*-butylamine. Mass spectrum (MALDI, *m/z*): 647.1920 (calculated for M^+ 647.3472); 548.2195 (calculated for MH^+ 648.3550). IR spectrum (KBr), ν, cm^{-1}: 1736 (ester $\nu_{C=O}$), 1703 ($\nu_{C=O}$ of keto group in exocycle), 1628 (amide I), 1616 ("chlorin bond"), 1551 (amide II). ^{1}H NMR spectrum, δ, ppm: 9.51 s (1H, H^{10}), 9.38 s (1H, H^5), 8.60 s (1H, H^{20}), 8.00 d.d [1H, 3-(C*H*=CH$_2$), *J* 19.5 and 11.5 Hz], 6.97 t [1H, 13(2)-CON*H*(CH$_2$)$_3$, *J* 5.5 Hz], 6.30 d.d [1H, 3-(CH=CHH$_{trans}$), *J* 18.1 and 1.5 Hz], 6.19 d.d [1H, 3-(CH=CHH$_{cis}$), *J* 11.6 and 1.4 Hz], 6.10 s [1H, H$^{13(2)}$], 4.56 br.d.t (1H, H^{17}, *J* 8.5 and 1.8 Hz), 4.43 q.d (1H, H^{18}, *J* 7.4 and 1.8 Hz), 3.70 s [3H, 17-(CH$_2$CH$_2$COOC*H*$_3$)], 3.61 s (3H, 12-CH$_3$), 3.42 s (3H, 2-CH$_3$), 3.24 s (3H, 7-CH$_3$), 3.68 q [2H, 6-(C*H*$_2$CH$_3$), *J* 7.0 Hz], 3.57–3.43 m [2H, 13(2)-CONH·C*H*$_2$(CH$_2$)$_2$CH$_3$], 2.66–2.49 m [2H, 17-(C*H*$_2$CH$_2$·COOCH$_3$)], 2.34–2.11 m [2H, 17-(CH$_2$C*H*$_2$COOCH$_3$)], 1.91 d (3H, 18-CH$_3$, *J* 7.4 Hz), 1.71 t (3H, 8-CH$_2$C*H*$_3$, *J* 7.4 Hz), 1.52–1.38 m [4H, 13(2)-CONHCH$_2$·(C*H*$_2$)$_2$CH$_3$], 0.97 t [3H, 13(2)-CONH(CH$_2$)$_3$C*H*$_3$, *J* 7.3 Hz], 0.53 br.s (1H, I-NH), –1.61 br.s (1H, III-NH). Mass spectrum (MALDI), *m/z*: 647.1920 [*M*]$^+$ (calculated *M* 647.3472), 648.2195 [*M* – H]$^+$ (calculated *M* 648.3350).

Methylpheoforbide *a* 13(2)-N-hexylamide (IX). Treating 20 mg of methylpheoforbide *a* **I** with 0.03 ml of N-hexylamine gave 9 mg (50%) of amide **IX** as a dark blue powder.). IR spectrum (KBr), ν, cm^{-1}: 1736 (ester $\nu_{C=O}$), 1700 ($\nu_{C=O}$ of the exocyclic keto group), 1630 (amide-I), 1616 (chlorin band), 1550 (amide II). ^{1}H NMR spectrum, δ, ppm: 9.52 s (1H, H^{10}), 9.38 s (1H, H^5), 8.60 s (1H, H^{20}), 8.01 d.d [1H, 3-(C*H*=CH$_2$),

J 17.6 Hz and 11.4 Hz], 6.98 t [1H, 13(2)-CON*H*$(CH_2)_5$·CH_3, *J* 5.8 Hz], 6.30 br.d [1H, 3-(CH=CHH_{trans}), *J* 17.5 Hz], 6.19 br.d [1H, 3-(CH=CHH_{cis}), *J* 11.5 Hz], 6.10 s (1H, $H^{13(2)}$), 4.57 br.d.t (1H, H^{17}, *J* 9.0 and 1.5 Hz), 4.43 q.d (1H, H^{18}, *J* 7.1 and 1.5 Hz), 3.70 s [3H, 17-($CH_2CH_2COOCH_3$)], 3.61 s (3H, 12-CH_3), 3.42 s (3H, 2-CH_3), 3.24 s (3H, 7-CH_3), 3.68 m [2H, 8-(CH_2CH_3)], 3.54–3.43 m [2H, 13(2)-CONH$CH_2(CH_2)_4$·CH_3], 2.66–2.50 m [2H, 17-($CH_2CH_2COOCH_3$)], 2.33–2.12 m [2H, 17-($CH_2CH_2COOCH_3$)], 1.92 d (3H, 18-CH_3, *J* 7.9 Hz), 1.72 t (3H, 8-CH_2CH_3, *J* 7.3 Hz), 1.50–1.30 m [8H, 13(2)-CONHCH$_2(CH_2)_4CH_3$], 0.90 t [3H, 13(2)-CONH$(CH_2)_5CH_3$, *J* 7.0], 0.54 br.s (1H, I-NH), –1.60 br.s (1H, III-NH). Mass spectrum (MALDI, *m/z*) 675.3715 (calculated for M^+ 675.3785); 676.3693 (calculated for $[M + H]^+$ 676.3863.

Methylpheoforbide *a* 13(2)-*N*-octylamide (X). Treating 50 mg of methylpheoforbide a **I** with 0.2 ml of *N*-octylamine gave 34 mg (53%) of amide **X**. IR spectrum (KBr), ν, cm^{-1}: 1736 (ester $\nu_{C=O}$), 1697 ($\nu_{C=O}$ of the exocyclic keto group), 1650 (amide I), 1616 (chlorin band), 1551 (amide II). ^{1}H NMR spectrum, δ, ppm: 9.49 s (1H, H^{10}), 9.35 s (1H, H^5), 8.58 s (1H, H^{20}), 7.97 d.d [1H, 3-(CH=CH$_2$), *J* 17.8 and 11.6 Hz], 6.96 t [1H, 13(2)-CON*H*$(CH_3)_5CH_3$, *J* 5.6], 6.28 d.d [1H, 3-(CH=CHH_{trans}), *J* 17.8 and 1.4 Hz], 6.17 d.d [1H, 3-(CH=CHH_{cis}), *J* 11.6 and 1.4 Hz], 6.09 s (1H, $H^{13(2)}$), 4.56 br.d.t (1H, H^{17}, *J* 8.9 and 1.5 Hz), 4.42 q.d (1H, H^{18}, *J* 7.2 and 1.5 Hz), 3.68 s [3H, 17-($CH_2CH_3COOCH_3$)], 3.60 s (3H, 12-CH_3), 3.40 s (3H, 2-CH_3), 3.21 s (3H, 7-CH_3), 3.68 m [2H, 8-(CH_2CH_3)], 3.54–3.43 m [2H, 13(2)-CONHCH$_2(CH_2)_4CH_3$], 2.64–2.49 m [2H, 17-($CH_2CH_2COOCH_3$)], 2.32–2.12 m [2H, 17-($CH_2CH_2COOCH_3$)], 1.91 d (3H, 18-CH_3, *J* 7.2 Hz), 1.69 t (3H, 8-CH_2CH_3, *J* 7.6 Hz), 1.48–1.24 m [8H, 13(2)-CONHCH$_2(CH_2)_6CH_3$], 0.88 t (3H, 13(2)-CONH$(CH_2)_7CH_3$, *J* 6.9], 0.52 br.s (1H, I-NH), –1.61 br.s (1H, III-NH). Mass spectrum (MALDI, *m/z*): 703.2933 (calculated for M^+ 703.4098); 704.3187 (calculated for $[M + H]^+$ 704.4176); 726.4061 (calculated for $[M + Na]^+$ 726.3995).

Methylpheoforbide *a* 13(2)-*N*,*N*-diethylamide (XI). Treating 50 mg of methylpheoforbide *a* **I** with 0.07 ml of diethylamine gave 27 mg (56%)of amide **XI** as a dark blue powder. IR spectrum (KBr), ν, cm^{-1}: 1736 (ester $\nu_{C=O}$), 1693 ($\nu_{C=O}$ in keto group of exocycle), 1638 (amide I), 1616 (chlorin band). ^{1}H NMR spectrum, δ, ppm: 9.51 s (1H, H^{10}), 9.38 s (1H, H^5), 8.57 s (1H, H^{20}), 8.00 d.d [1H, 3-(C*H*=CH$_2$), *J* 17.8 and 11.6 Hz], 6.66 s [1H, $H^{13(2)}$], 6.28 d.d [1H, 3-(CH=CHH_{trans}), *J* 17.8 and 1.4 Hz], 6.17 d.d [1H, 3-(CH=CHH_{cis}), *J* 11.6 and 1.4 Hz], 4.45 q.d (1H, H^{18}, *J* 7.3 and 1.4 Hz), 4.18 br.d.t (1H, H^{17}, *J* 8.1 and 1.5 Hz), 3.67 s [3H, 17-($CH_2CH_2COOCH_3$)], 3.50 s (3H, 12-CH_3), 3.41 s (3H, 2-CH_3), 3.24 s (3H, 7-CH_3), 3.83–3.57 m [6H, 8-(CH_2CH_3), 13(2)-CON(CH_2CH_3)$_2$], 2.70–2.42 m [2H, 17-($CH_2CH_2COOCH_3$)], 2.41–2.20 m [2H, 17-($CH_2CH_2COOCH_3$)], 1.80 d (3H, 18-CH_3, *J* 7.2 Hz), 1.70 t (3H, 8-CH_2CH_3, *J* 7.6 Hz), 1.36 t [6H, 13(2)-CON$(CH_2CH_3)_2$, *J* 8.0 Hz], 0.46 br.s (1H, I-NH), –1.67 br.s (1H, III-NH). Mass spectrum (MALDI, *m/z*): 647.7866 (calculated for M^+ 647.3472), 679.3384 (calculated for $[M + Na]^+$ 6703369).

Methylpheoforbide *a* 13(2)-piperidide (XII). Treating 50 mg of methylpheoforbide *a* **I** with 0.07 ml of piperidine gave 20 mg (37%) of amide **XII** as a dark blue powder. IR spectrum (KBr), ν, cm^{-1}: 1736 (ester $\nu_{C=O}$), 1695 ($\nu_{C=O}$ of the exocyclic keto group), 1635 (amide I), 1616 (chlorin band). ^{1}H NMR spectrum, δ, ppm: 9.53 s (1H, H^{10}), 9.41 s (1H, H^5), 8.58 s (1H, H^{20}), 8.03 d.d [1H, 3-(C*H*=CH$_2$), *J* 17.9 and 11.6 Hz], 6.75 s [1H, $H^{13(2)}$], 6.31 d.d [1H, 3-(CH=CHH_{trans}), *J* 17.6 and 1.6 Hz], 6.20 d.d [1H, 3-(CH=CHH_{cis}), *J* 11.7 and 1.4 Hz], 4.47 q.d (1H, H^{18}, *J* 7.4 and 2.8 Hz), 4.40–3.51 m [11H, H^{17}, 13(2)-CONHC$_5H_{10}$], 3.69 s [3H, 17-($CH_2CH_2COOCH_3$)], 3.55 s (3H, 12-CH_3), 3.43 s (3H, 2-CH_3), 3.27 s (3H, 7-CH_3), 3.70–3.63 m [2H, 8-(CH_2CH_3)], 2.66–2.51 m [2H, 17-(CH_2CH_2·$COOCH_3$)], 2.40–2.16 m [2H, 17-($CH_2CH_2COOCH_3$)]. 1.87 d (3H, 18-CH_3, *J* 7.2 Hz), 1.72 t (3H, 8-CH_2CH_3, *J* 7.8 Hz), 0.48 br.s (1H, I-NH), –1.63 br.s (1H, III-NH). Mass spectrum (MALDI, *m/z*): 659.2062 (calculated for M^+ 659.3472), 660.2312 (calculated for $[M + H]^+$ 659.3550).

Methylpheoforbide *a* 13(2)-morpholide (XIII). Treating 50 mg of methylpheoforbide a **I** with 0.07 ml of morpholine gave 9 mg (17%) of amide **XIII** as a dark blue powder. IR spectrum (KBr), ν, cm^{-1}: 1736 (ester $\nu_{C=O}$), 1694 ($\nu_{C=O}$ of the exocyclic keto group), 1645 (amide I), 1618 (chlorin band). ^{1}H NMR spectrum, δ, ppm: 9.50 s (1H, H^{10}), 9.38 s (1H, H^5), 8.57 s (1H, H^{20}), 8.00 d.d [1H, 3-(C*H*=CH$_2$), *J* 17.6 Hz and 11.3 Hz], 6.68 s [1H, $H^{13(2)}$], 6.29 d.d [1H, 3-(CH=CHH_{trans}), *J* 17.7 and 1.0 Hz], 6.19 d.d [1H, 3-(CH=CHH_{cis}), *J* 11.6 and 1.0 Hz], 4.44 q.d (1H, H^{18}, *J* 7.4 and 1.7 Hz), 4.35–3.62 m [9H, H^{17}, 13(2)-CONC$_4H_8$O], 3.67 s [3H, 17-($CH_2CH_2COOCH_3$)], 3.63 s (3H, 12-CH_3), 3.41 s (3H, 2-CH_3), 3.25 s (3H, 7-CH_3), 3.70–3.63 m [2H, 8-(CH_2CH_3)], 2.66–2.51 m

[2H, 17-($CH_2CH_2COOCH_3$)], 2.40–2.16 m [2H, 17-($CH_2CH_2COOCH_3$)], 1.87 d (3H, 18-CH_3, *J* 6.9 Hz), 1.71 t (3H, 8-CH_2CH_3, *J* 7.6 Hz), 0.50 br.s (1H, I-NH), –1.63 br.s (1H, III-NH). Mass spectrum (MALDI, *m/z*): 661.2022 (calculated for M^+ 661.3264), 662.2127 (calculated for $[M + H]^+$ 662.3343).

ACKNOWLEDGMENTS

The work was carried out with the support of Federal Agency of Science and Innovations (state contract no. 02.740.11.0081); with the support of Russian Academy of Sciences (project no. 09-i-3-2004).

REFERENCES

1. Spikes, J.D., J. *Photochem. Photobiol., (B),* 1990, vol. 6, no. 3, p. 259.
2. Sternberg, E.D., Dolphin, D., and Bruckner, C., *Tetrahedron*, 1998, vol. 54, no. 17, p. 4151.
3. Nyman, E.S. and Hynninen, P.H., *J. Photochem. Photobiol., (B),* 2004, vol. 73, nos. 1–2, p. 1.
4. *Porfiriny: struktura, svoistva, sintez* (Porphyrins: Structure, Properties, Synthesis), Enikolopyan, N.S., Ed., Moscow: Nauka, 1985.
5. Seely, G.R., *The Structure and Chemistry of Functional Groups*, in *The Chlorophylls*, Seely, L.P. and Vernon, C.R., Eds., New York: Acad. Press, 1966, p. 67.
6. Ellsworth, P.A. and Storm, C.B., *J. Org. Chem*., 1978, vol. 43, no. 2, p. 281.
7. Belykh, D.V., Karmanova, L.P., Spirikhin, L.V., and Kutchin, A.V., *Mendeleev Commun*., 2002, vol. 12, p. 77.
8. Belykh, D.V., Karmanova, L.P., Spirikhin, L.V., and Kuchin, A.V., *Zh. Org. Khim*., 2007, vol. 43, no. 1, p. 120.
9. Ma, L. and Dolphin, D., *Tetrahedron*, 1996, vol. 52, no. 3, p. 849.
10. Weller, A. and Livingston, R., *J. Am. Chem. Soc.,* 1954, vol. 76, no. 6, p. 1575.
11. Pennington, F.C., Boettcher, N.B., and Katz, J.J., *Bioorg. Chem*., 1974, vol. 3, no. 2, p. 204.
12. Belykh, D.V. and Kutchin, A.V., *Khimiya v Interesakh Ustoichivigi Razvitiya*, 2008, vol. 16, p. 617.
13. Belykh, D.V., Tarabukina, I.S., Gruzdev, I.V., Kodess, M.I., and Kutchin, A.V., *J. Porphyrins and Phthalocyanines*, 2009, vol. 13, nos. 8–9, p. 949.
14. Palm, V.A., *Vvedenie v teoreticheskuyu organicheskuyu khimiyu* (Introduction to the Theoretical Organic Chemistry), Moscow: Vysshaya Shkola, 1974.
15. Osuka, A., Wada, U., and Shinoda, S., *Tetrahedron*, 1996, vol. 52, no. 12, p. 4311.